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Observation of the Infrared Spectrum in Supersonic Free Jet Expansion with Time Resolved FTIR Spectroscopy: The Spectrum of C_2F_6

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The system to observe FTIR spectrum in supersonic free jet expansion was made and the spectra of C_2F_6 were observed both in a pulsed jet expansion and in a continuous jet expansion. The behavior in the pulsed jet was analyzed from the observed time resolved spectrum. The sharp peaks of ν_1 and ν_7 free from the disturbance due to hot bands were found at 1117.1cm^{-1} and 1252.8cm^{-1} , respectively. The temperature of the molecule in a pulsed jet was found to be about 6K from a band shape analysis.

Introduction

Supersonic free jet expansion has been widely used in molecular science to produce molecules of very low temperature and produce clusters of molecules. Many interesting results¹⁾ have been published in vibrational spectroscopy on the behavior of molecules at very cold temperature or the nature of molecular clusters by combining the technique of pulsed supersonic jet and the infrared diode laser spectroscopy. However, the continuous tuning range of infrared diode laser is typically less than 1cm^{-1} due to mode hops, and therefore, it is not easy to observe the spectrum with wide frequency range or to obtain whole band shape of heavy molecules.

High resolution Fourier Transform Infrared Spectroscopy (FTIR) is another good tool by which precise frequencies and intensities of absorption lines and spectra of wide frequency range can be obtained easily. The observation of transient species such as free radicals and molecular ions²⁾, and the dynamic behavior of molecule with time resolved technique³⁾ have been reported by this method. The investigation on the behavior in supersonic jet expansion by FTIR will be another target since by supersonic jet technique the molecule can be easily cooled to very low temperature from which the spectra free from the hot bands can be obtained. Several works⁴⁾ have been performed and simplified spectra of relatively heavy molecules have been observed to resolve each rotation-vibration lines to obtain precise molecular constants⁵⁾.

The knowledge on precise infrared band intensities of fluorocarbons will be important for the estimation of green house effect. The vibrational spectra of these molecules, however, have not been well understood because of disturbance due to hot bands of low-lying vibrational mode such as torsional motion. Not only the center frequencies but also the integrated intensities of the infrared bands of these relatively heavy molecules depend largely

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on the temperature. To obtain the infrared spectra of these molecules which is free from the effect of the hot bands, the technique of the supersonic free jet expansion seems to be a good method when combined with the FTIR spectroscopic technique.

The FTIR spectra of C_2F_6 , one of a fluorocarbon, have been observed in a pulsed jet with time resolved technique and also in a continuous flow jet. Two observed spectra have been compared with each other and the behavior in a jet has been discussed in this report.

Experimental

A BOMEM DA3.36 FTIR spectrometer was used for the observation of the spectra. Infrared light was taken out from the spectrometer, led into the vacuum chamber where the supersonic jet was generated, and then detected by a liquid nitrogen cooled HgCdTe detector.

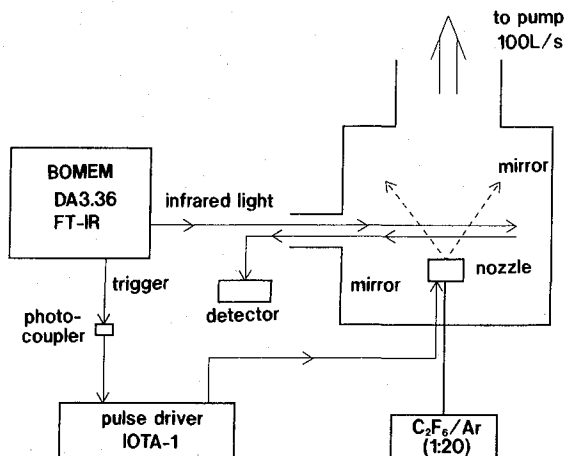


Figure 1. A schematic diagram of the experimental apparatus.

Fig. 1 shows the diagram of the experimental setup. A White type multi-reflection mirror system was used to obtain longer optical path length. The distance between the nozzle head and infrared light was changed by moving the nozzle head. The optimum distance was found to be 5mm from the signal strength. Assuming that the diameter of the jet is 5mm, the effective optical path length was estimated to be about 20mm. The chamber was evacuated by a roots pump (ULVAC 006C) and a rotary pump with flow rate of 100 ℓ / s (measured by a flow meter). The sample gas mixture ($C_2F_6:Ar=1:20$) was prepared in a high pressure vessel (8atm) at least two hours before the measurement.

A continuous jet expansion was generated by passing the sample of 2.5 atm through a nozzle with diameter of 200 μ m. A pulsed jet expansion was made by regulating the gas flow with a pulse valve (General Valve, $d=0.8$ mm) and a pulse driver (IOTA-1). The gas pressure was set to 3atm, and the valve was opened for 200 μ s. This valve operation was controlled by a trigger from the FTIR spectrometer for the observation of a time resolved spectrum. In this operation the use of photocoupler was necessary to avoid the electric noise

due to the pulse driver.

The time resolved FTIR technique similar to previous work^{3,6)} was used to observe the spectrum of C_2F_6 in the pulsed jet expansion. Fig. 2 shows the timing chart of the data sam-

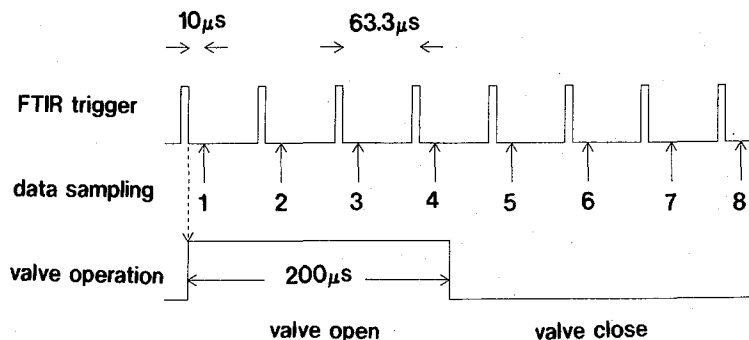


Figure 2. The timing chart of the FTIR trigger (zero-cross of He-Ne laser), FTIR D/A trigger and pulse valve operation.

pling of the FTIR and the opening and closing of the pulse valve. The spectrum was measured by the use of TRV5 system supplied by BOMEM. The cycle time of FTIR depends on the velocity of the moving mirror. In this experiment, it was set to 0.5cm/s which gives the cycle time of $63.3\mu s$. The signal from the infrared detector was sampled at the time shown by arrows in Fig. 2, and the spectra at the time after opening the valve

$$\Delta t = 10 + 63.3(n-1)\mu s, n=1-16$$

could be obtained in one measurement. Since the data sampling scheme shown in Fig. 2 should be done at all the data points required for the Fourier transformation, and since the cycle of the pulse valve operation was limited to 100Hz , 157 scans were necessary to observe the whole data points. The measuring time as long as 4 hours were necessary for the accumulation of 16 interferograms at the resolution of 1cm^{-1} .

An ab initio MO calculation (Gaussian 92⁷⁾) with the basis set of 4-31G* has been carried out to estimate the molecular constants of C_2F_6 and derived parameters are given in Table 1.

Table 1. The molecular parameters of C_2F_6 calculated by 4-31G* basis set.

	4-31G*	obs.
$r(\text{CC})/\text{\AA}$	1.524	1.545 ^a
$r(\text{CF})/\text{\AA}$	1.3101	1.326 ^a
$\alpha(\text{CCF})/\text{degree}$	109.74	109.8 ^a
A/cm^{-1}	0.9726	
B/cm^{-1}	0.6338	
ν_1/cm^{-1}	1246	1117 ^b
ν_7/cm^{-1}	1438	1253 ^b
ζ_7	0.865	

a. Reference 8)

b. present result.

Results and Discussion

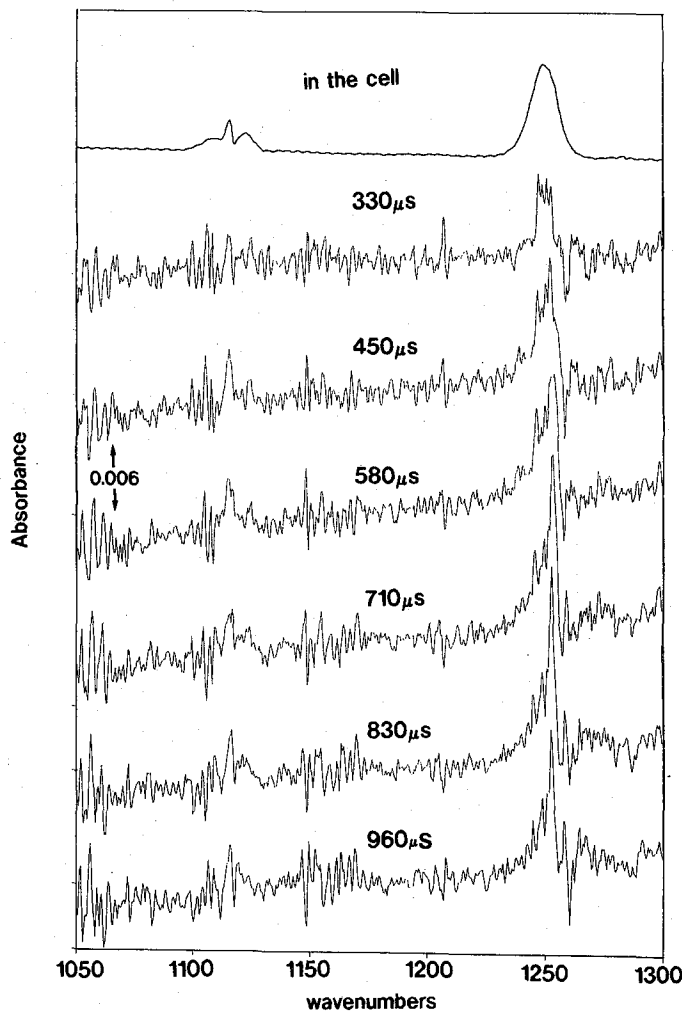


Figure 3. Time resolved FTIR spectra of C_2F_6 in pulsed supersonic jet. The time cited in the figure is that after the trigger for opening the valve.

Fig. 3 shows the time resolved FTIR spectra of C_2F_6 in the pulsed supersonic molecular jet. The valve was operated at 100Hz and opened for 200 μs in each cycle. The pressure of the vacuum chamber was found to be about 5mTorr when the pulse valve was operated at 100Hz. The resolution of the spectra was $1cm^{-1}$, and the spectrum was accumulated for 80 times. It took about 20 hours for each observation. The time quoted in Fig. 3 is the time after the trigger to open the pulse valve. Spectra measured earlier than 300 μs after the trigger showed no signal due to the supersonic jet but the absorption of C_2F_6 remained in the cell. A sharp peak appears at $1253cm^{-1}$ in the spectrum measured at 550 μs after the trigger. The peak position is found slightly higher than that observed at room temperature and shows that

C_2F_6 molecule was really cooled in the supersonic jet expansion. This also shows that the pulsed jet reached to the optical path region $550\ \mu s$ after the valve was opened. The signal becomes stronger with time, and the maximum absorption was obtained at $830\ \mu s$. Since the distance between the nozzle and optical path was about 5mm, there must be a dead time of about several hundred micro seconds before the gas blows into the cell if the velocity of the jet is assumed to be 300m/s.

The observed peak positions of $\nu_1(A_{1g})$ and $\nu_7(E_u)$ are found to be 1116.8 and 1252.8 cm^{-1} , respectively and the shifts from the frequencies observed at room temperature are 1.1 and 3.4 cm^{-1} , respectively. These shifts reflect that the molecule in the jet is cooled and the spectrum in the jet is free from the hot bands. The band becomes sharper with the time as is seen in the figure and shows the decrease in temperature of molecule. This will be discussed later.

By the pulsed jet expansion technique we can cool down the gas sample easily with the vacuum system of ordinary pumping ability. However in time resolved FTIR spectroscopy, very long accumulation time is required to obtain the spectrum with good S/N ratio, and when much higher resolution is required it is actually impossible. For high resolution FTIR spectroscopy, the use of a continuous jet should be considered instead of a pulsed jet.

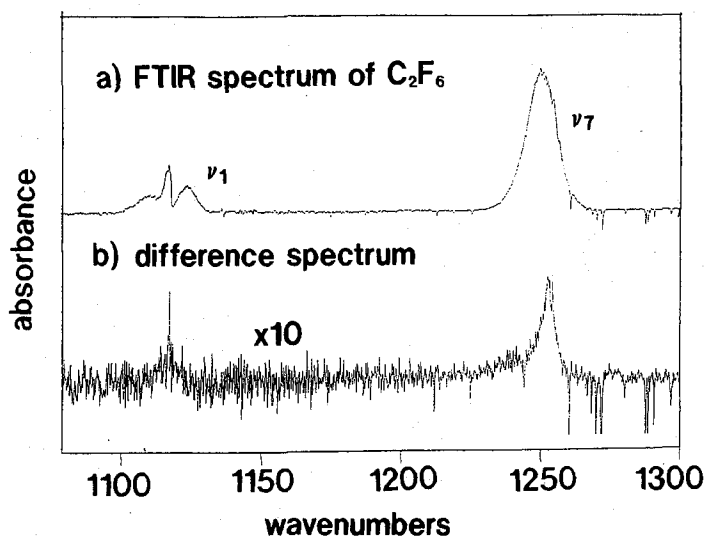


Fig. 4 FTIR spectra of C_2F_6 in a continuous supersonic jet.

Fig. 4 shows the FTIR spectrum of C_2F_6 in a continuous supersonic free jet expansion. A nozzle with a diameter of $200\ \mu m$ was used and the sample gas pressure was set to 2.5atm. Since large amount of sample gas was flowed into the chamber in this case, the pressure in the chamber became high, and found to be about 30mTorr. The distance between the nozzle and the optical path was set to 5mm. When it was longer than 10mm, the spectrum of C_2F_6 at low temperature was not observed at all. The spectrum was measured at the resolution of $0.2cm^{-1}$. The time required for 256 accumulation was about 30minutes which is much shorter than that required for time resolved measurement. Since the pressure in the vacuum chamber was rather high, the observed absorption reflect the thermalization of

C_2F_6 in the chamber. The spectrum due to cooled C_2F_6 in the supersonic jet can be deduced by subtracting the spectrum measured at room temperature.

The peak positions of ν_1 and ν_7 were 1117.1 and 1252.7 cm^{-1} , respectively. Both of them shifted to higher wavenumbers from those observed at room temperature, and they agreed well with the frequencies observed in the pulsed jet. The Q-branch of ν_1 at 1117.1 cm^{-1} shows much sharper peak than that in pulsed jet since higher resolution was used for the observation in continuous jet.

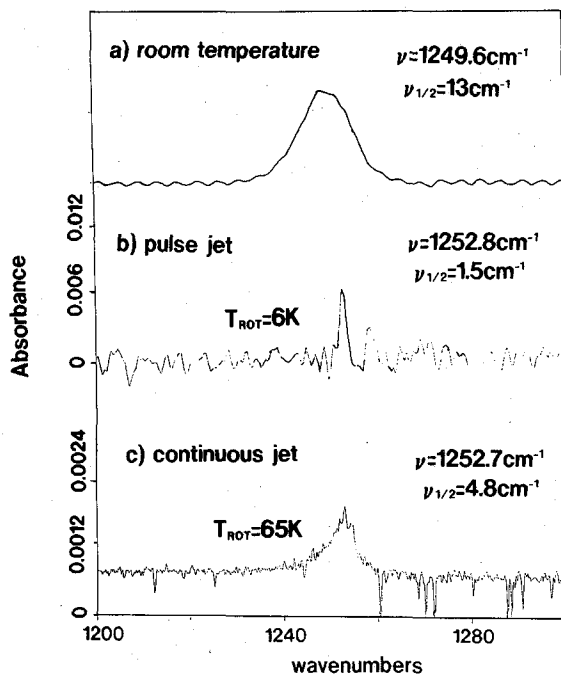


Fig. 5 FTIR spectra of C_2F_6 in supersonic jets .a) in the cell. b) in the pulsed jet. Rotational temperatures T_{ROT} were estimated from the band widths.

Figs. 5a), 5b), and 5c) show the spectra of the ν_7 band of C_2F_6 observed at room temperature, in the pulsed jet, and in the continuous jet, respectively. The observed peak positions and band widths of them are given in Table 2.

Table 2. Peak frequencies (ν_1 and ν_7) and band width (ν_7) of C_2F_6 .

	room temperature	pulsed jet	continuous jet
ν_1/cm^{-1}	1115.7	1116.8	1117.1
ν_7/cm^{-1}	1249.4	1252.8	1252.7
$\Delta \nu_7/cm^{-1}$	13	1.8	4.8
T_{ROT}/K		6	65

As is seen from the table, the band width becomes narrower when the jet was used. The temperatures of the molecule (rotational temperature: T_{ROT}) were estimated by simulating the band shape of the ν_7 band. Since there is no experimental data about the molecular constants determined by high resolution spectroscopy, ab initio values of the molecular parameters were used in the calculation. This band is E-type band and its band shape largely depends on the Coriolis constant $\zeta_7^{(9)}$. It was estimated from the I_x matrix elements calculated by ab initio MO method (see Table 1). In the band shape calculation, the rotational constants A, B were fixed to those of ab initio values, and the effect of α_A , α_B , and centrifugal distortion constants were neglected. The rotational temperature was changed step by step so as to well reproduce the experimental band width. It was found that the rotational temperatures of C_2F_6 in pulsed and continuous jets were 6K and 65K, respectively. The temperature of C_2F_6 in the continuous jet was considerably higher than that in the pulsed jet. This is due to the higher background pressure in the vacuum chamber and smaller diameter of the orifice in the case of continuous jet.

The calculated band width for room temperature was 10 cm^{-1} , which is considerably smaller than the observed value 13 cm^{-1} . This discrepancy comes from the disturbance due to hot bands in the observed spectrum. Since the peak value shifted from the true band center to the lower frequency by 3 cm^{-1} because of the absorption due to hot bands, the apparent band width should also increase by 3 cm^{-1} .

The effective concentration of C_2F_6 in the supersonic jet was estimated to be 200mTorr as follows. The absorption intensity of C_2F_6 in the continuous jet was about 5% of that remained in the chamber. Since the total optical path in the chamber was nearly 1.5m and effective path was estimated to be 2cm, the effective pressure should be about 100mTorr in the continuous jet. On the other hand, the peak intensity of C_2F_6 in the pulsed jet was 5 times stronger than that in the continuous jet, and the band width of the former was about one third of the latter. The effective concentration of C_2F_6 in the pulsed jet is therefore estimated to be about 200mTorr. Although the formation of C_2F_6 dimer in the pulsed jet would be expected, no evidence was found in the spectrum because of poor S/N ratio of the system, and therefore this effect was neglected in the above estimation.

Conclusion

The FTIR spectrum of C_2F_6 in a pulsed supersonic free jet expansion was observed by FTIR spectroscopic technique. A part of the behavior of molecule in pulsed jet became clear by the observation of time resolved spectrum. The spectrum free from the disturbance due to hot bands was obtained. The continuous supersonic molecular jet method seems to be better than the pulsed jet for the observation of high resolution FTIR spectrum although large amount of sample is required for the observation and larger vacuum system ($> 2000\text{ l/s}$) will be required to produce much colder molecule.

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Erratum

**Observation of the Infrared Spectrum in Supersonic Free
Jet Expansion with Time resolved FTIR Spectroscopy :
The Spectrum of C₂F₈**

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Page 142, Table 1:

A/cm⁻¹ 0.9726 and B/cm⁻¹ 0.6338 should read A/cm⁻¹ 0.09726 and B/cm⁻¹ 0.06338,
respectively.